Methylsulfonyl Radical Unimolecular Dissociation Studied by Deep-UV Ultrafast Photoionization Spectroscopy†

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The secondary dissociation dynamics of the methylsulfonyl radical following the photodissociation near 193 nm of methylsulfonyl chloride and methylsulfonyl ethanol has been studied using femtosecond mass-resolved photoionization spectroscopy. The primary dissociation is instrument-limited (<200 fs) for both precursors. The methylsulfonyl unimolecular dissociation is measured to have a lifetime of 0.34 ps with complete secondary dissociation following methylsulfonyl chloride photolysis. For the case of methylsulfonyl ethanol, the measured lifetime is 1.1 ps and ~40% of the radical remains undissociated for the 18 ps duration of the experiment. We have successfully modeled the experimental results assuming an impulsive dissociation process to yield the internal energy distributions in the primary photoproducts and RRKM calculations based on structures and energetics of the methylsulfonyl radical obtained from the literature.

Introduction

Dimethyl sulfide, released by marine biota, is the largest natural component of the global sulfur flux.[1] Its subsequent atmospheric oxidation by OH and NO_3 leads, in part, to products that can produce new sulfate particles that act as cloud condensation nuclei. A global mechanism for dimethyl sulfide oxidation was developed from a consideration of the available kinetic and mechanistic information by Yin et al. in 1990.[2] The salient feature of this mechanism is a series of oxidation steps that proceed toward a branching between methane sulfonic acid, CH_3SO_3H, and sulfate, SO_4^{-2}. Measurements of the product ratios as a function of latitude indicate that this branching is very temperature dependent. Barone et al.[3] suggested that the competition between the thermal decomposition of adducts such as methylsulfonyl radical, CH_3SO_2, and their bimolecular reactions with atmospheric species could be the source of the strong temperature dependence of the observed branching. They reasoned that the bimolecular reactions are relatively temperature independent while the unimolecular decompositions have large activation energies and thus steep temperature dependencies. Branching controlled by the ratio of these processes would be strongly temperature dependent. Saltelli and Hjorth[4] also discussed the importance of CH_3SO_2 to the branching ratio.

There have been a number of theoretical[5−9] and experimental[7−10] investigations of the methylsulfonyl radical over the past 15 years. Davis[5] used SCF, MP2 and MP4 calculations to determine the geometries and relative energies of methylsulfonyl and its oxygen-bonded isomer methoxysulfinyl, CH_3OSO, which he found to be about 10 kcal mol^{-1} more stable. Laakso et al.[6] did similar calculations on the species HSO_2 and HOSO; HSOO; and HOOS and used these results to derive energetics for CH_3SO_2 and CH_3OSO. Recently, Frank and Turecek[7] and Kukui et al.[8] reported detailed calculations of the structure and energetics of both the methylsulfonyl radical and the transition state along the path to dissociation to $CH_3 + SO_2$. This allowed them to use RRKM theory to calculate kinetic parameters for the reverse addition of $CH_3 + SO_2$ and, with some assumptions about collisional efficiencies, the unimolecular lifetime of methylsulfonyl.

The lifetime toward unimolecular dissociation of the methylsulfonyl radical has been measured in a low-pressure discharge-flow study[10] and with a pair of discharge-flow and pulsed laser photolysis systems spanning the pressure range from 1 to 600 Torr[8] by Le Bras and co-workers. Neither system represented a direct measurement of the lifetime. Sequential formation and destruction reactions were important and rate constants were derived from model fits to observed profiles of species such as CH_3S, CH_3O, and SO_2. In their first paper, this group reported a decay rate in 1 Torr of He of 510 ± 150 s^{-1}. In the later paper, with more constraining observations and a more complete model, they were able to place an upper limit of 100 s^{-1} on the rate under the same conditions.

In view of the importance of the rate of the unimolecular dissociation, we attempted to directly measure the decay of photolysis-produced methylsulfonyl using cavity ring-down absorption spectroscopy near 350 nm, where the peak of the CH_3SO_2 liquid-phase absorption has been observed by Chatgilialoglu et al.[9] This method of measuring unimolecular dissociation rates is always susceptible to errors arising from the residual internal energy of the radical. If the decay rate is at the high end of that determined by the indirect studies, the thermalization time and decomposition time are close and the results are difficult to interpret unambiguously. The photolysis precursor must be carefully chosen to minimize residual internal energy in the product radical. In fact, we were never able to observe absorption attributable to CH_3SO_2 when we used methylsulfonyl chloride, CH_3SO_2Cl (MSC), as the photolytic precursor.

To sort out the photolysis dynamics of MSC and resolve the question of its suitability as a precursor for CH_3SO_2, we have undertaken an ultrafast product study of the dissociation of both MSC and methanesulfonyl ethanol, CH_3SO_2EtOH (MSE), using photoionization as a direct probe of CH_3SO_2. We have previously shown for the case of acetyl radical photoproduct from acetone[11] and other precursors[12] that ultrafast photodissociation

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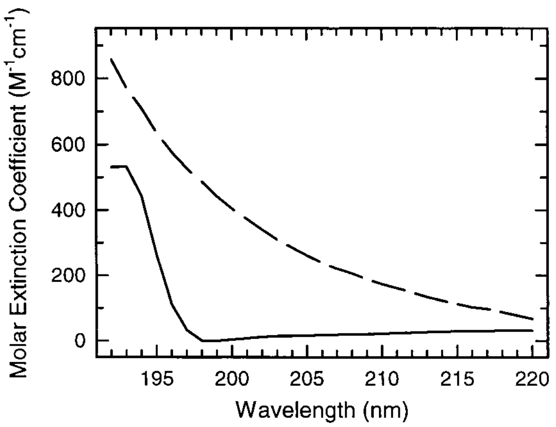

Figure 1. Absorption spectra measured for methylsulfonyl chloride (dashed line) and methylsulfonyl ethanol (solid line) at a pressure of 1 Torr.

studies with photoionization detection have great utility for determining product channels and unimolecular decomposition rates of radicals and, on the basis of these, inferring details about the statistical nature of the dissociation. In this paper we report measurements of the prompt dissociation lifetime and undissociated fraction of methylsulfonyl radical following photolysis near 193 nm of two likely precursors for the radical. Using the previously calculated structures and energetics of the radical, we infer details of the dissociation dynamics.

Experimental Section

The apparatus for measuring mass-resolved ultrafast photoionization has been described previously,[11] so only a brief account will be presented here. It consists of a Ti:sapphire regeneratively amplified laser system (Positive Light Spitfire pumped by a Merlin and seeded by a Clark oscillator pumped by a Spectra-Physics Millenia) for generating ~120 fs, 0.5 mJ pulses near 780 nm at a 3 kHz repetition rate. The deep-UV pump (195 nm) and near-UV (260 nm) probe pulses are generated by three successive stages of nonlinear mixing using BBO. The deep-UV and near-UV pulse energies are approximately 3 and 10 μJ, respectively. The collinear pump and probe pulses are focused with a 25-cm focal length lens into a chamber in which the sample gas is slowly flowed at a pressure of about 5×10^{-5} Torr. Photoions are mass-resolved using a quadrupole mass spectrometer. The probe beam is chopped at one-half the laser repetition rate of the laser and the detected photoion current is measured with a lock-in amplifier. No photoion current is detected in the absence of the pump beam. Temporal delay between the pulses is controlled with a motorized translation stage on the probe beam. The instrumental time resolution is ~350 fs, as determined by photoionization signals measured for rapidly dissociating gases, such as dichloroethylene.

Absorption spectra were measured in a 10 cm long cell under static conditions with pressures near 1 Torr. Methylsulfonyl chloride and methylsulfonyl ethanol were used as received from Aldrich.

Results and Discussion

Conventional absorption spectra were measured for both MSC and MSE (Figure 1) primarily to optimize the excitation wavelength. The spectra indicate that the MSC absorption starts around 250 nm and gradually increases to about 600 M^{-1} cm^{-1} at 195 nm. This agrees with the published spectrum in this region by Kozlowski et al.[13] MSE, on the other hand, exhibits a much sharper and somewhat shorter wavelength absorption onset at 195 nm. At 194 nm the extinction of MSC is about twice that of MSE. Consequently, the ultrafast photoionization studies were carried out with the pump wavelength at 196 nm for MSC and at 194 nm for MSE.

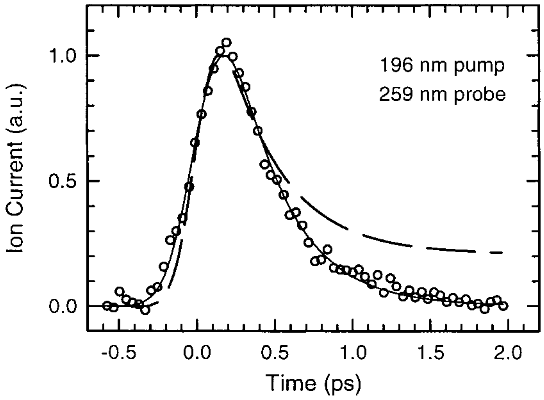

Figure 2. Photoionization decay curve measured for methylsulfonyl following photodissociation of methylsulfonyl chloride. The points are the data and the solid line is a fit to a single-exponential decay with a time constant of 0.34 ps. None of the radical intermediate remains undissociated after 2 ps. The dashed curve is calculated from a model assuming impulsive energy partitioning in the parent dissociation and a statistical/RRKM decomposition for methylsulfonyl radical as described in the text.

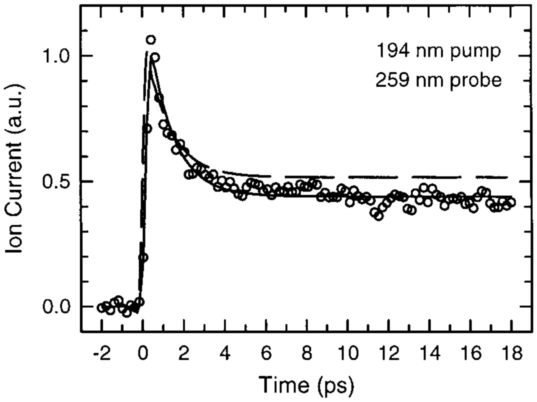

Figure 3. Photoionization decay curve measured for methylsulfonyl following photodissociation of methylsulfonyl ethanol. The points are the data and the solid line is a fit to a single-exponential decay with a time constant of 1.1 ps for the portion (sixty percent) of the methylsulfonyl radicals that dissociate within 18 ps. The dashed curve is calculated from a model assuming impulsive energy partitioning in the parent dissociation and a statistical/RRKM decomposition for methylsulfonyl radical as described in the text.

The primary results of this study are the photoionization curves measured for MSC and MSE. Our focus will be on the secondary dissociation dynamics for methylsulfonyl, but decay times were also measured for the parent molecules. The decay curves (not shown) for detecting the parent/precursor photoions (at $m/z = 114$ for MSC and $m/z = 124$ for MSE) are both instrument-limited (<200 fs). These results indicate very short parent excited-state lifetimes in both cases.

The photoionization curves obtained by detecting the methylsulfonyl photoion ($m/z = 79$) are shown in Figure 2 for MSC and in Figure 3 for MSE for deep-UV excitation (near 195 nm) and UV probe (near 260 nm). The signals reflect the time dependence of the secondary dissociation, corresponding to the unimolecular dissociation of the methylsulfonyl radical intermediate. On the time scale of interest (~1 ps) and for the pressures used, there are no changes in the internal energy of the intermediate. The signals are well-described by single exponential decays (plus a persistent component for MSE). The ionization potential for methylsulfonyl has been reported to be 8.67 eV.[14] Since the probe photons (260 nm) have an energy of 4.77 eV, the signals for methylsulfonyl are likely due to a one-photon pump and two-photon probe process. The decay times derived are 0.34 ps for MSC and 1.1 ps for MSE. The curves also indicate that while there is no undissociated methylsulfonyl (<2%) from the MSC photodissociation, there is ~40% undissociated methylsulfonyl from MSE on the time scale of the experiment (18 ps). There is no evidence of any other contribution to the signals, such as from dissociative ionization of the parent ion. Also, in this case, since the secondary dissociation rate is longer than the parent photodissociation rate, the signal due to dissociative ionization of the parent does not complicate the analysis.

One goal of this study is to search for a photolytic precursor which produces stable methylsulfonyl. Upon inspection of the photoionization curves in Figures 2 and 3 it is evident that after 18 ps about half the methylsulfonyl produced from photodissociation of MSE remains undissociated, while none is observed for MSC. The decay time of methylsulfonyl from MSE is longer than 18 ps, but it may be shorter than what is required for a unimolecular or bimolecular reaction experiment. This is unlikely, however. RRKM calculations by Kukui et al.[8] show that methylsulfonyl radicals produced below the barrier to dissociation collisionally thermalize.

The relative amounts of undissociated methylsulfonyl are what one might expect. In the MSC photodissociation the companion fragment to methylsulfonyl is an atom, so that all the internal energy resides in the methylsulfonyl radical. In the case of MSE, the EtOH fragment can carry away some if not more internal energy than methylsulfonyl, assuming the same type of primary energy partitioning in both cases. A lower methylsulfonyl internal energy distribution produced from MSE yields a larger fraction below the methylsulfonyl dissociation barrier.

To evaluate a *possible* mechanism for the primary and secondary dissociations in the photodissociation of MSC and MSE, the observed methylsulfonyl dissociation rates and fractional dissociations will be compared to calculated values. There are no experimental product studies of the photodissociation of MSC or MSE that would provide information on the primary dissociation energy partitioning. Consequently, a measurement of the methylsulfonyl dissociation rate k_{uni}(methylsulfonyl) is not sufficient to determine the nature of the methylsulfonyl unimolecular dissociation; i.e., without information on the methylsulfonyl internal energy, the k_{uni}(methylsulfonyl) cannot be interpreted to indicate whether the dissociation is statistical or not. Nevertheless, as a starting point, we have calculated methylsulfonyl dissociation rates based on assumed, limiting case energy partitioning and RRKM model unimolecular dissociation.

To calculate the methylsulfonyl dissociation rate, the bond dissociation energy (BDE) is needed to obtain the available energy (E_{avl}). The methylsulfonyl internal energy distribution is obtained by assuming an impulsive model for the primary dissociation energy partitioning. RRKM calculations are performed for the radical using the results of calculations for the dissociation barrier and vibrational frequencies and structures for the ground and transition states of methylsulfonyl.

The bond dissociation energy for MSC has been reported as 70 ± 3 kcal/mol by Chatgilialoglu et al.[14] Using this value, E_{avl} ($=h\nu -$ BDE) for MSC is 75.8 kcal/mol. Chatgilialoglu et al.[15] have also investigated a series of substituted sulfonyl chlorides (alkyls and aryls) and found very similar BDE values. Although the substitution is not the same for MSE, we have assumed the same BDE for MSE, resulting in a E_{avl} of 77.3 kcal/mol.

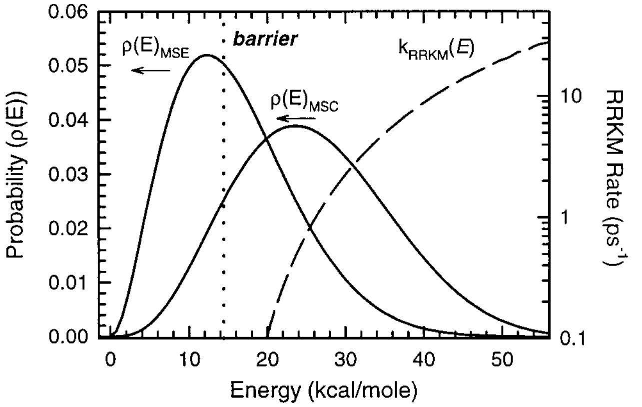

Figure 4. Calculated methylsulfonyl internal energy distributions following photodissociation of methylsulfonyl ethanol and methylsulfonyl chloride near 195 nm (solid lines) and calculated RRKM unimolecular dissociation rates (dashed line).

The internal energy of the methylsulfonyl radical intermediate depends on the energy partitioning in the primary dissociation. In the absence of an experimental determination of this partitioning and the methylsulfonyl internal energy, we have used an impulsive model,[16] which favors translational energy, and a statistical/prior model,[17] which predicts more internal energy. The impulsive model predicts that for MSC, 31.1% (23.5 kcal/mol) of E_{avl} is partitioned into the internal energy of methylsulfonyl and for MSE, 16.2% (12.5 kcal/mol). The prior model on the other hand, predicts the methylsulfonyl internal energy to be 66 kcal/mol for MSC and 34 kcal/mol for MSE. These models yield average energies for translational and internal energies; a more realistic treatment is to generate a distribution function for the internal energy. One approach that has been used previously in several studies of acetyl cyanide[12,18] is to model the internal energy distribution $\rho(E)$ of the intermediate as a binomial function of the form

$$\rho(E_{int}) = [E_{avl} - E_{trans} - E_{int}(X)](E/E_{avl})^a(1 - E/E_{avl})^b$$

where E_{trans} is the total average translational energy and $E_{int}(X)$ is the average internal energy for the companion fragment (Cl for MSC, for which $E_{int}(X) = 0$, and CH_2CH_2OH for MSE). The exponents are chosen to normalize the function. The calculated $\rho(E_{int})$ probabilities for methylsulfonyl based on an impulsive model partitioning for MSC and MSE are shown in Figure 4. These distributions can then be used to calculate the fraction of undissociated methylsulfonyl as well as to calculate the distribution-averaged RRKM rate.

Given the methylsulfonyl internal energy based on the partitioning models, the methylsulfonyl unimolecular RRKM dissociation rates ($k_{RRKM}(E)$) were calculated with the UNIMOL program[19] using calculated molecular parameters, such as the barrier and ground and transition state vibrational frequencies. The energetics for the methylsulfonyl dissociation have been calculated by Davis[5] at the MP2 level for both the ground and transition states and by Frank and Turecek (MP2 and B3LYP).[7] The calculations are in relatively good agreement, indicating a dissociation energy of about 14 kcal/mol and a 1−1.5 kcal/mol barrier to recombination. The latter is similar to the recombination barrier of 1.5 kcal/mol measured by Good and Thynne.[20]

TABLE 1: Observed and Calculated Results for Dissociation Rates and Undissociated Fraction of Methylsulfonyl for Photodissociation of MSC and MSE[a]

	MSC		MSE	
	calcd	obsd	calcd	obsd
$\langle E\rangle$, kcal/mol	26.9		16.4	
$\langle E;E > E_{\mathrm{bar}}\rangle$, kcal/mol	29.18		22.9	
$1/\langle k\rangle$, ps	0.39	0.34	1.04	1.14
% undiss	13	<2	53	40

[a] The calculations are based on impulsive energy partitioning in the primary dissociation. Rates are calculated using E_{bar} =14.4 kcal/mol and $\langle k\rangle_{\mathrm{calc}} = \langle k(E)\rho(\mathrm{E})\rangle$.

Structures and vibrational frequencies for the ground and transition states were also reported by Davis[5] and Frank and Turecek.[7] For the RRKM calculations we used the results of Frank and Turecek for structures and vibrational frequencies and a dissociation barrier of 14.4 kcal/mol. The barrier (E_{bar}) and calculated ρ(E) permit the fraction of undissociated methylsulfonyl from MSC and MSE to be calculated from

$$\int \rho(\mathrm{E} < 14.4\ \mathrm{kcal/mol})/\int \rho(\mathrm{E})$$

The results of the impulsive partitioning model are listed in Table 1. The prior model predicts no undissociated methylsulfonyl. Frank and Turecek[7] also reported calculated RRKM rates for the methylsulfonyl dissociation and, as expected, the rates we obtain are very similar to theirs. The calculated rates $k_{\mathrm{RRKM}}(E)$ are plotted in Figure 4. As we described in previous work,[12] the distribution averaged rate $\langle k\rangle$ can be calculated in a manner that includes the internal energy-dependent rate using $\langle k\rangle = \langle k(E)\rho(\mathrm{E})\rangle$. This is a better approximation than simply considering the rate at the average internal energy ($k(\langle E\rangle)$, for $E > E_{\mathrm{bar}}$). The distribution averaged rate, $\langle k(E)\rho(\mathrm{E})\rangle$, yields results that are substantially closer to the explicit sum of exponentials at each energy. For methylsulfonyl in the internal energy range appropriate to the present case, the rate calculated by $\langle k(E)\rho(\mathrm{E})\rangle$ is 2−3 times faster than $k(\langle E\rangle)$, as can be seen in Figure 4.

The observed and calculated dissociation rates and undissociated fraction are presented in Table 1 for the calculations based on the impulsive model for primary energy partitioning. Also included are the calculated average internal energies, both for the entire distribution and for the part that is above the barrier. The calculated values are very close to those observed, especially for the rate and the fraction undissociated for MSE. In contrast, a prior model for the primary dissociation is very different than the observed results. The prior predicts no undissociated methylsulfonyl and dissociation rates that are much too fast. For MSC and MSE, $\langle \mathrm{E}_{\mathrm{prior}}\rangle = 66$ and 34 kcal/mol, corresponding to unimolecular RRKM lifetimes of 22 and 240 fs, which are much faster than the observed rates.

The impulsive partitioning calculations agree with the observed values within 20%, except for the fraction undissociated of methylsulfonyl from MSC. These results may also reflect the uncertainty in the BDE, which propagates to about 5% in the fractional dissociation and 15% in the calculated rate; other uncertainties in the calculations include those in the barrier height and ab initio parameters used in the RRKM calculations. Alternatively, this might be explained by a methylsulfonyl internal energy distribution narrower than the one generated by the calculations. Since a substantial fraction of the methylsulfonyl radical from MSE is undissociated, we have some information about the methylsulfonyl internal energy distribution. Since almost half the methylsulfonyl radicals remain intact and if the distribution is not too asymmetric, the center or average should be close to the barrier energy, which is the case for the calculated $\langle E\rangle$. The calculations suggest that our results for the photodissociation of MSC and MSE are consistent with a primary energy partitioning followed by a statistical RRKM type unimolecular dissociation of methylsulfonyl. However, without an experimental determination of the primary partitioning and the internal energy of methylsulfonyl, these observed rates could be due to various combinations of primary and secondary dissociation mechanisms.

Unimolecular studies have recently been carried out for similarly sized molecules and rarely are the results compatible with simple limiting-case partitioning and statistical intermediate unimolecular dissociation. It does appear that there is a higher propensity for statistical unimolecular behavior for intermediates formed from prompt/direct primary dissociation (such as observed for acetyl cyanide and acetic acid)[12] than for those produced by predissociation (such as for acetyl from the 3s Rydberg state of acetone),[11] although in none of these cases is the primary energy partitioning well-described by the impulsive model. The molecular behavior may conform to a simple model when the companion fragment is simple, e.g., an atom as for MSC. In the present case, however, the more complicated molecule, MSE, agrees better with the simple impulsive calculation in not only the rate but also the fraction undissociated.

Summary

We have studied the photodissociation dynamics of MSC and MSE with particular attention to the secondary dissociation of the methylsulfonyl radical. We have shown that MSE photodissociation at 193 nm, where the absorption is large, results in about 40% undissociated methylsulfonyl on the time scale of our experiment (18 ps). Thus, MSE photodissociation is a good candidate for the production of methylsulfonyl for kinetic studies.

Of course, the unknown of primary importance in atmospheric models is the unimolecular lifetime of methylsulfonyl under ambient atmospheric conditions. This is a very difficult rate to measure directly. It can be obtained from indirect studies such as those reported by Le Bras and co-workers[8,10] or derived from modeling studies. The results reported here can be used to validate such models. We have determined a decay rate and undissociated fraction of methylsulfonyl produced from two photolytic precursors. If the translational energy of the Cl partner from MSC photodissociation were known, a better estimate of the methylsulfonyl internal energy would allow a more rigorous test of the RRKM rates derived from the calculated structures and energetics. Similarly, a better understanding of the product energy distributions in MSE photodissociation would be useful.

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